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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the gas barrier property film which made the gas barrier property coat agent and it which have the gas barrier property which was excellent under high humidity form in the front face of a thermoplastics film as a coat.

[0002]

[Description of the Prior Art] Since thermoplastics films, such as a polyamide film and polyester film, are excellent in reinforcement, transparency, and a moldability, they are used for the application broad as wrapping. However, since these thermoplastics films have large gas permeability, such as oxygen, when it is used for the package of common food and retorting food etc., while saving for a long period of time, deterioration of food may arise by gas, such as oxygen which penetrated the film.

[0003] Then, the emulsion of a polyvinylidene chloride (it outlines Following PVDC) etc. was coated on the surface of thermoplastics, and the laminated film in which the PVDC layer with high gas barrier property was made to form has been broadly used for food packing etc. However, since PVDC generates organic substances, such as a sour gas, at the time of incineration, while the interest about an environment increases in recent years, shift to other ingredients is desired strongly.

[0004] Although polyvinyl alcohol (it outlines Following PVA) does not have generating of a toxic gas on the other hand as an ingredient which changes to PVDC, either and the gas barrier property under a low humidity ambient atmosphere is also high, gas barrier property cannot fall rapidly as humidity becomes high, and it cannot use for the package of the food containing moisture etc. in many cases.

[0005] As a polymer which has improved the fall of the gas barrier property under the high humidity of PVA, although the copolymer (EVOH) of vinyl alcohol and ethylene is known In order to maintain the gas barrier property in high humidity on practical use level in this polymer, it is necessary to make the content of ethylene to some extent high. It becomes refractory in water, to consider as a coating ingredient, it is necessary to use the mixed solvent of an organic solvent, or a water and an organic solvent, such a polymer is not desirable from a viewpoint of an environmental problem, and since it needs the recovery process of an organic solvent etc., it has the problem of becoming cost quantity.

[0006] As an approach of carrying out the coat of the liquefied constituent which consists of a water-soluble polymer to a film, and making gas barrier property high also under high humidity discovering By carrying out the coat of the water solution which consists of a partial neutralization object of PVA, polyacrylic acid, or polymethacrylic acid to a film, and heat-treating it Although the approach of constructing a bridge by the ester bond in both polymers was proposed (JP,10-237180,A), by this approach, in order to fully advance esterification and to raise the gas barrier property of a film, heating of long duration is required of an elevated temperature, and the problem was in productivity. Since a film colors and an appearance is spoiled by furthermore carrying out a long duration reaction at an elevated temperature, an improvement is required for food packing.

[0007] It is known widely that the polymer which the technique which deck-watertight-luminaire-izes PVA by constructing a bridge using a cross linking agent is variously known from the former, for

example, contains a maleic-acid unit will react with hydroxyl groups, such as PVA and polysaccharide, and will be deck-watertight-luminaire-ized. For example, having the water resisting property the layer which consists of a 25 - 50% partial neutralization object of an isobutylene-maleic-anhydride copolymer and PVA excelled [ water resisting property ] in JP,8-66991,A is known. Moreover, the approach of deck-watertight-luminaire-izing the film of PVA is described to JP,49-1649,A by by mixing an alkyl vinyl ether-maleic-acid copolymer to PVA.

[0008] However, deck-watertight-luminaire-izing (namely, nonaqueous vitrification) and gas barrier property are different properties, although deck-watertight-luminaire-ized by generally constructing a bridge in a polymer molecule, gas barrier property is a property which prevents invasion and diffusion of oxygen etc. of a comparatively small molecule, even if it only constructs a bridge in a polymer, it does not restrict that gas barrier property is obtained, for example, as for three-dimensions cross-linking polymers, such as an epoxy resin and phenol resin, it does not have gas barrier property.

[0009]

[Problem(s) to be Solved by the Invention] The reactant high barrier property coat agent which raised productivity is offered to the above problems, by applying this coat agent, also under high humidity, it has high gas barrier property and, as for this invention persons, coloring also tends to offer few gas barrier property films.

[0010]

[Means for Solving the Problem] this invention persons reached [ that the above-mentioned technical problem is solvable and ] header this invention wholeheartedly by applying the coat agent containing a specific resin constituent on the surface of a film, and making the layer which consists of this resin constituent form as a result of research. That is, the summary of this invention is as follows.

(1) The drainage system gas barrier property coat agent which the weight ratio of polyvinyl alcohol and an ethylene-maleic-acid copolymer becomes from 97 / 3 - 10/90.

(2) The gas barrier property film in which the coat which consists of a coat agent of the above-mentioned (1) publication was formed on one [ at least ] front face of a thermoplastics film.

[0011]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail.

[0012] If it is with the thermoplastics film used in this invention, the layered product of polyolefine films, such as polyester film, such as polyamide films, such as nylon 6, Nylon 66, and Nylon 46, polyethylene terephthalate, polyethylenenaphthalate, polybutylene terephthalate, and polybutylene naphthalate, polypropylene, and polyethylene, or those films may be mentioned, and an unstretched film or an oriented film is sufficient. Moreover, corona treatment of the front face of a film may be carried out, and the anchor coat may be carried out to the film.

[0013] As an approach of manufacturing a film, thermoplastics is heated and fused with an extruder, it extrudes from a T die, cooling solidification is carried out with a cooling roller etc., an unstretched film is obtained, or extrude from a circular die, it is made to solidify with water cooling or air cooling, and an unstretched film is obtained. When manufacturing an oriented film, once rolling round an unstretched film, the coincidence biaxial extending method or the approach of extending by the biaxial extending method serially is continuously desirable. From engine-performance sides, such as the mechanical property of a film, and thickness homogeneity, the approach of combining the flat type producing-film method and the tenter extending method by the T die is desirable.

[0014] The weight ratio of polyvinyl alcohol and an ethylene-maleic-acid copolymer in this invention needs 97 / 3 - 10/90, and to be the range of 90 / 10 - 40/60 preferably. Especially when separating from this range, crosslinking density required in order to make the gas barrier property of the film under a high humidity ambient atmosphere discover cannot be obtained, and the gas barrier property film made into the purpose of this invention cannot be obtained.

[0015] PVA used in this invention can obtain the polymer of vinyl ester using completeness or well-known approaches, such as carrying out partial saponification. As vinyl ester, formic acid vinyl, vinyl acetate, propionic-acid vinyl, vinyl pivalate, BASA tic acid vinyl, etc. are mentioned, and vinyl acetate is industrially the most desirable especially.

[0016] It is the range which does not spoil the effectiveness of this invention, and it is also possible to copolymerize other vinyl compounds to vinyl ester. As other vinyl system monomers, partial saturation dicarboxylic acid, such as partial saturation monocarboxylic acid, such as a crotonic acid, an acrylic acid, and a methacrylic acid, and the ester of those, a salt, an anhydride, an amide, nitril, and a maleic acid, an itaconic acid, a fumaric acid, and the salt of those, the alpha olefins of carbon numbers 2-30, alkyl vinyl ether, and vinyl pyrrolidone are mentioned.

[0017] In this invention, in order to give gas barrier property to a film front face, as for the polymer by which a laminating is carried out, considering as water solubility is desirable on production, and since water solubility will be spoiled if a hydrophobic copolymerization component is made to contain so much, it is not desirable.

[0018] In addition, the approach of using the alkali saponifying method well-known as the saponification approach and the acid saponifying method, and carrying out alcoholysis in a methanol especially using hydroxylation alkali is desirable. If whenever [ saponification ] is so desirable that it is close to 100% from a viewpoint of gas barrier property and whenever [ saponification ] is too low, barrier property ability will fall. whenever [ saponification ] -- usually -- about 90% or more -- desirable -- 95% or more -- it is -- average degree of polymerization -- 200-2500 -- the thing of 200-2000 is preferably good.

[0019] The ethylene-maleic-acid copolymer used in this invention is obtained by carrying out the polymerization of a maleic anhydride and the ethylene by well-known approaches, such as a solution radical polymerization. Moreover, it is also possible to carry out little copolymerization of other vinyl compounds in the range which does not spoil the purpose of this invention. The compound which has the olefins of the carbon numbers 3-30, such as vinyl ester, such as acrylic ester, such as a methyl acrylate, methacrylic acid methyl, an ethyl acrylate, methacrylic acid ethyl, butyl acrylate, and methacrylic acid butyl, formic-acid vinyl, and vinyl acetate, styrene, p-styrene sulfonic acid, a propylene, and an isobutylene, the hydroxyl group of PVA, etc. and the reactant radical that reacts as a vinyl compound can be mentioned.

[0020] the maleic-acid unit in the ethylene-maleic-acid copolymer in this invention -- more than 10 mol % -- containing is desirable. If there are few maleic-acid units than ten-mol %, formation of the structure of cross linkage by the reaction with a PVA unit will be inadequate, and gas barrier property will fall.

[0021] In addition, in dryness, the maleic-acid unit in the ethylene-maleic-acid copolymer used by this invention tends to serve as maleic-anhydride structure which the contiguity carboxyl group cyclodehydrated, and on the other hand, in the time of humidity, or a water solution, ring breakage of it is carried out and it serves as maleic-acid structure.

[0022] In this invention, it is desirable 0.1 - 30 weight section and to carry out 1-20 weight section combination of PVA and the component to which the weight ratio of an ethylene-maleic-acid copolymer has cross-linking in the mixture 100 weight section of 97 / 3 - 10/90 which form a gas barrier layer preferably. The gas barrier property which was excellent in 200 degrees C with heat treatment of a short time for about 15 seconds can be made to discover by blending a bridge formation component. It is not desirable, in order that sufficient bridge formation effectiveness cannot be acquired, and a cross linking agent may check the manifestation of gas barrier property conversely when [ than 30 weight sections ] more when the addition of a cross linking agent is under the 0.1 weight section.

[0023] As a cross linking agent used in this invention, the cross linking agent which has self-cross-linking is sufficient, and a metal complex with the coordination position of the compound or many \*\* which have two or more carboxyl groups and/or hydroxyl groups, and functional groups that react in intramolecular etc. is sufficient. Specifically, an isocyanate compound, a melamine compound, a urea compound, an epoxy compound, a carbodiimide compound, a zirconium salt compound, etc. are desirable. Moreover, you may use it combining these cross linking agents.

[0024] By mixing an inorganic stratified compound to the coat agent in this invention, the gas barrier property of a film can be raised further. An inorganic stratified compound is an inorganic compound which a unit crystal layer laps and forms the layer structure, and swelling and the thing which carries out cleavage are desirable especially in a solvent.

[0025] As a desirable example of an inorganic stratified compound, a montmorillonite, beidellite, Saponite, hectorite, a saunconite, a vermiculite, a fluorine mica, A muscovite, a palagonite, phlogopite, a biotite, lepidolite, margarite, A klint night, ANANDAITO, chlorite, a DOMBA site, SUDOAITO, KUKKEAITO, chestnut NOKUROA, a chamosite, Nima Ito, a TETORASHI lyric mica, There are talc, pyrophyllite, nacrite, a kaolinite, halloysite, a chrysotile, a sodium TENIO light, xanthophyllite, antigorite, dickite, a hydrotalcite, etc., and a bloating tendency fluorine mica or especially a montmorillonite is desirable.

[0026] Even if it produces naturally, these inorganic stratified compounds may compound or denaturalize artificially, and may process them with the organic substance, such as an onium salt.

[0027] A bloating tendency fluorine mica system mineral is the most desirable in respect of a whiteness degree, and is shown by the degree type.

$\alpha(\text{MF})$  and  $\beta(a\text{MgF}_2 \text{ and } b\text{MgO}) - \gamma\text{SiO}_2$  (M expresses sodium or a lithium among a formula, and  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $a$ , and  $b$  express a multiplier respectively, and are  $0.1 \leq \alpha \leq 2$ ,  $2 \leq \beta \leq 3.5$ ,  $3 \leq \gamma \leq 4$ ,  $0 \leq a \leq 1$ ,  $0 \leq b \leq 1$ , and  $a+b=1$ .)

[0028] As a manufacturing method of such a bloating tendency fluorine mica system mineral, oxidation silicon, a magnesium oxide, and various fluorides are mixed, the mixture is fused completely [ in a 1400-1500-degree C temperature requirement ] all over an electric furnace or a gas furnace, for example, and there is the so-called scorification which carries out crystal growth of the fluorine mica system mineral into a reaction container by the cooling process.

[0029] Moreover, there is a method of carrying out the intercalation of the alkali-metal ion to this, and obtaining a bloating tendency fluorine mica system mineral, using talc as starting material (JP,2-149415,A). By this approach, \*\* fluoride alkali or fluoride alkali is mixed to talc, and it is abbreviation within a magnetic crucible. A bloating tendency fluorine mica system mineral can be obtained by carrying out short-time heat-treatment at 700-1200 degrees C.

[0030] Under the present circumstances, as for the amount of the \*\* fluoride alkali mixed with talc, or fluoride alkali, it is desirable to consider as 10 - 35% of the weight of the range of the whole mixture, and since the generation yield of a bloating tendency fluorine mica system mineral falls in separating from this range, it is not desirable.

[0031] As for the alkali metal of \*\* fluoride alkali or fluoride alkali, considering as sodium or a lithium is desirable. Such alkali metal may be used independently and may be used together. Moreover, in the case of a potassium, a bloating tendency fluorine mica system mineral is not obtained among alkali metal, but it uses together with sodium or a lithium, and if it is the limited amount, using in order to adjust bloating tendency is also possible.

[0032] Furthermore, in the process which manufactures a bloating tendency fluorine mica system mineral, it is also possible to adjust the bloating tendency of the bloating tendency fluorine mica system mineral which carries out little combination of the alumina and generates it.

[0033] A montmorillonite is shown by the degree type and can be obtained by refining what is produced naturally.

$\text{MaSi}_4(\text{aluminum}_{2-a}\text{Mg}_a)\text{O}_{10}(\text{OH})_2n\text{H}_2\text{O}$  (M expresses the cation of sodium among a formula and  $a$  is 0.25-0.60.) Moreover, since the number of the water molecules combined with the ion-exchange nature cation between layers may change according to conditions, such as a cation kind and humidity, it is expressed with  $n\text{H}_2\text{O}$  in a formula.

Moreover, the isomorphism ion substitution product of the MAGUNE cyanogen montmorillonite expressed with degree formula group, an iron montmorillonite, and an iron MAGUNE cyanogen montmorillonite also exists in a montmorillonite, and these may be used.

$\text{MaSi}_4(\text{aluminum}_{1.67-a}\text{Mg}_{0.5+a})\text{O}_{10}(\text{OH})_2, n\text{H}_2\text{OMaSi}_4(\text{Fe}_{2-a}\text{Mg}_a)\text{O}_{10}(\text{OH})_2$ , and  $n\text{H}_2\text{OMaSi}_4(\text{Fe}_{1.67-a}\text{Mg}_{0.5+a})\text{O}_{10}(\text{OH})_2$  (M expresses the cation of sodium among a formula and  $a$  is 0.25-0.60.)

[0034] Usually, although a montmorillonite has ion-exchange nature cations, such as sodium and calcium, between the layer, the content ratio changes with places of production. In this invention, it is desirable that the ion-exchange nature cation between layers is permuted by sodium by ion exchange

treatment etc. Moreover, it is desirable to use the montmorillonite refined by elutriation processing.

[0035] In the coat agent of this invention, unless the property is spoiled greatly, a thermostabilizer, an antioxidant, reinforcement, a pigment, a degradation inhibitor, a weathering agent, a flame retarder, a plasticizer, a release agent, lubricant, etc. may be added.

[0036] As a thermostabilizer, an antioxidant, and a degradation inhibitor, hindered phenols, phosphorus compounds, hindered amine, a sulfur compound, a copper compound, the halogenides of alkali metal, or such mixture are mentioned, for example.

[0037] As a reinforcement, clay, talc, a calcium carbonate, zinc carbonate, straw SUTONAITO, a silica, an alumina, a magnesium oxide, a calcium silicate, a sodium aluminate, sodium aluminosilicate, a magnesium silicate, glass balun, carbon black, a zinc oxide, a zeolite, a hydrotalcite, a metal fiber, a metal whisker, a ceramic whisker, a potassium titanate whisker, boron nitride, graphite, a glass fiber, a carbon fiber, etc. are mentioned, for example.

[0038] furthermore, to the coat agent of this invention, by using together a cross linking agent and an inorganic stratified compound, gas barrier property can be boiled markedly and can be raised.

[0039] In case PVA and the ethylene-maleic-acid copolymer in this invention are mixed and a water solution is prepared, it is desirable to add 1-40Eq of % of alkali compounds preferably to the carboxyl group in an ethylene-maleic-acid copolymer% 0.1-50Eq. although an ethylene-maleic-acid copolymer can be used as a water solution even if the hydrophilic property of itself will be high and will not add alkali, if there are many amounts of copolymerization of a maleic acid, by carrying out proper amount addition of the alkali compound, the gas barrier property of the film obtained boils it markedly, and improves. The hydroxide of alkali metal or alkaline earth metal, ammonium hydroxide, an organic ammonium hydroxide compound, etc. are mentioned that what is necessary is just what can neutralize the carboxyl group in an ethylene-maleic-acid copolymer as an alkali compound.

[0040] What is necessary is just to carry out by the well-known approach as the adjustment approach of a water solution using the dissolution iron pot equipped with the agitator etc. For example, the method of using PVA and an ethylene-maleic-acid copolymer as a water solution separately, and mixing and using them before use is desirable. At this time, the stability of a water solution improves by what the alkali compound is added to the water solution of an ethylene-maleic-acid copolymer for. Moreover, it is better for solubility to add alkali first, although PVA and an ethylene-maleic-acid copolymer may be added to the water in a dissolution iron pot. Moreover, little addition of alcohol or the organic solvent can also be carried out at water for the purpose, such as compaction of the purpose which raises solubility, or a desiccation process, and an improvement of the stability of a solution.

[0041] In order to raise the gas barrier property of the film of this invention, it is required between PVA and an ethylene-maleic-acid copolymer for the crosslinking reaction by the ester bond to occur, but the catalyst of an acid etc. can also be added in order to promote crosslinking reaction.

[0042] In order to raise the gas barrier property of a film enough, as for the thickness of the gas barrier coat in this invention, it is desirable to make it thicker than at least 0.1 micrometers. Moreover, although the polymer concentration at the time of carrying out the coat of the gas barrier-coating-sealant agent to a film is suitably changed with the viscosity of liquid, or the specification of reactivity and the equipment to be used, it becomes difficult to carry out the coat of the layer of thickness sufficient with a too much thin solution to discover gas barrier property, and it tends to produce the problem of requiring long duration in a subsequent desiccation process. On the other hand, when the concentration of a solution is too high, a problem may be produced in mixed actuation, shelf life, etc. As for such a viewpoint to polymer concentration, it is desirable to make it 5 - 50% of the weight of the range of the whole solution.

[0043] Although especially the approach of coating a film with a gas barrier property coat agent is not limited, the usual approaches, such as gravure roll coating, reverse roll coating, and wire bar coating, can be used. It may coat, after supplying a tenter type drawing machine, extending and (coincidence biaxial extension) heat-treating a film the transit direction and crosswise at coincidence, after coating an unstretched film first and drying, in order to perform coating in advance of extension, or extending in the transit direction of a film using a multistage hot calender roll etc., and you may extend crosswise by

the tenter type drawing machine after desiccation (serially biaxial extension). Moreover, it is also possible to combine extension of the transit direction and the coincidence biaxial extension by the tenter.

[0044] In this invention, in order to carry out crosslinking reaction of the ethylene-maleic-acid copolymer to PVA, it is preferably desirable to heat-treat in an ambient atmosphere 180 degrees C or more still more preferably 150 degrees C or more the temperature of 120 degrees C or more. If heat treatment temperature is low, crosslinking reaction cannot fully be advanced, and it becomes difficult for the film which has sufficient gas barrier property to obtain. If heat treatment time amount is too short not much, crosslinking reaction cannot fully be advanced, and it becomes difficult for the film which has sufficient gas barrier property to obtain. Usually, 3 seconds or more are preferably good 1 second or more.

[0045] In this invention, since the gas barrier property of a film changed with the class of base material film, thickness, and the thickness of a coat layer, it evaluated the oxygen transmission coefficient of the coat layer itself. It asked for the oxygen transmission coefficient from the following type.

$1/QF=1/QB+L/PC$ , however QF: Oxygen transmittance of a coated film (ml/m<sup>2</sup> and day-MPa)

QB: Oxygen transmittance of a thermoplastics film (ml/m<sup>2</sup> and day-MPa)

PC: The oxygen transmission coefficient of a coat layer (ml-mu m/m<sup>2</sup> and day-MPa)

L: Coat bed depth (micrometer)

Therefore, if PC and L understand the oxygen transmittance of a coated film, it can be estimated from an upper type. Oxygen barrier property measured the oxygen transmittance in 20 degrees C and the ambient atmosphere of 85% of relative humidity with the Mocon oxygen barrier measuring instrument. In addition, the oxygen transmittance of a PET film with a thickness of 12 micrometers made the oxygen transmittance of 900 ml/m<sup>2</sup>, day-MPa, and a nylon 6 film with a thickness of 15 micrometers 400 ml/m<sup>2</sup> and day-MPa.

[0046]

[Example] Next, an example explains this invention concretely.

[0047] Example 1PVA (UF040 whenever [ G and saponification ] made in Unitika Chemical, 99%, average degree of polymerization 400) was dissolved in pure water, and 10% of the weight of the water solution was obtained. The ethylene-maleic-acid alternating copolymer (the product made from ALDRICH, weight average molecular weight 100,000-500,000) was dissolved in the water which contains five-mol % of a sodium hydroxide to the carboxyl group of a maleic acid, and it considered as 10% of the weight of the water solution. The water solution was mixed, it stirred and coat liquid was obtained so that the weight ratio of PVA and an ethylene-maleic-acid copolymer might become 70/30. The coat was carried out by MEIYABA so that the paint film thickness after drying this coat liquid on a biaxial extension PET film (Emblet PET 12 by Unitika, Ltd., thickness of 12 micrometers) might be set to about 2 micrometers, and after drying for 2 minutes at 100 degrees C, it heat-treated for 15 seconds at 200 degrees C. The appearance of the obtained coated film did not have coloring, either, it was good and the coat layer was insoluble in water. Moreover, the oxygen transmittance in 20 degrees C and 85%RH was 88 ml/m<sup>2</sup> and day-MPa, and the oxygen transmission coefficients of a coat layer were 195 ml-mu m/m<sup>2</sup> and day-MPa.

[0048] The same actuation as an example 1 was performed except having changed whenever [ examples 2-4, weight ratio / of 11PVA and an ethylene-maleic-acid copolymer /, or neutralization ], as shown in Table 1. The coat layer of the obtained coated film was insoluble in water. The oxygen transmittance of a coated film and the oxygen transmission coefficient of a coat layer were shown in Table 1.

[0049] The water solution was prepared so that the weight ratio of PVA and an ethylene-maleic-acid copolymer might become 70/30 by the same actuation as example 5 example 1, then to the solid content 100 weight section of PVA and an ethylene-maleic-acid copolymer, the melamine compound (Mitsui SAITEKKU, Cymel 325) was added so that it might become 5 weight sections, and it stirred, and coat liquid was prepared. The coat was carried out by MEIYABA so that the paint film thickness after drying this coat liquid on a biaxial extension PET film (Emblet PET 12 by Unitika, Ltd., thickness of 12 micrometers) might be set to about 2 micrometers, and after drying for 2 minutes at 100 degrees C, it



heat-treated for 15 seconds at 200 degrees C. The coat layer of the obtained coated film was insoluble in water. The oxygen transmittance of a coated film and the oxygen transmission coefficient of a coat layer were shown in Table 1.

[0050] The same actuation as an example 1 was performed except having changed the class and addition of six to example 10 cross linking agent, as shown in Table 1. The oxygen transmittance of the obtained coated film and the oxygen transmission coefficient of a coat layer were shown in Table 1.

[0051] The water solution was prepared so that the weight ratio of PVA and an ethylene-maleic-acid copolymer might become 70/30 by the same actuation as example 12 example 1, then to the solid content 100 weight section of PVA and an ethylene-maleic-acid copolymer, the inorganic stratified compound (the Kunimine Industries make, KUNIPIAF) was added so that it might become 10 weight sections, and it stirred, and coat liquid was prepared. The coat was carried out by MEIYABA so that the paint film thickness after drying this coat liquid on a biaxial extension PET film (Emblet PET 12 by Unitika, Ltd., thickness of 12 micrometers) might be set to about 2 micrometers, and after drying for 2 minutes at 100 degrees C, it heat-treated for 15 seconds at 200 degrees C. The oxygen transmittance of the obtained coated film and the oxygen transmission coefficient of a coat layer were shown in Table 1.

[0052] The water solution was prepared so that the weight ratio of PVA and an ethylene-maleic-acid copolymer might become 70/30 by the same actuation as example 13 example 1, then to the solid content 100 weight section of PVA and an ethylene-maleic-acid copolymer, it added so that it might become 10 weight sections about 5 weight sections and an inorganic stratified compound (the Kunimine Industries make, KUNIPIAF), and the melamine compound (Mitsui SAITEKKU, Cymel 325) was stirred, and coat liquid was prepared. The coat was carried out by MEIYABA so that the paint film thickness after drying this coat liquid on a biaxial extension PET film (Emblet PET 12 by Unitika, Ltd., thickness of 12 micrometers) might be set to about 2 micrometers, and after drying for 2 minutes at 100 degrees C, it heat-treated for 15 seconds at 200 degrees C. The oxygen transmittance of the obtained coated film and the oxygen transmission coefficient of a coat layer were shown in Table 1.

[0053] The coat was carried out by MEIYABA so that the paint film thickness after drying the coat liquid obtained in the example 14 example 1 on a biaxial extension nylon film (the emblem by Unitika, Ltd., thickness of 15 micrometers) might be set to about 2 micrometers, and after drying for 2 minutes at 100 degrees C, it heat-treated for 15 seconds at 200 degrees C. The oxygen transmittance of the obtained coated film and the oxygen transmission coefficient of a coat layer were shown in Table 1.

[0054] Using the extruder (the diameter of 75mm and ratio of length to diameter are the slow compression type monopodium screw of 45) equipped with the T die, example 15 PET was extruded in the shape of a sheet at the cylinder temperature of 260 degrees C, and the T-die temperature of 280 degrees C, was stuck on the cooling roller adjusted by the skin temperature of 10 degrees C, was quenched, and was used as the unstretched film with a thickness of 120 micrometers. Then, the coat liquid of the same presentation as an example 1 was coated so that an unstretched film might be led to a gravure roll type coating machine and the coat thickness after desiccation might be set to 20 micrometers, and it dried for 45 seconds in the 80-degree C hot blast dryer. Next, after supplying the film to the tenter type coincidence biaxial drawing machine and carrying out a preheating for 2 seconds at the temperature of 100 degrees C, it extended to the lengthwise direction at 95 degrees C, and extended by one 3.5 times the scale factor of this in 3 times and a longitudinal direction. Furthermore, at 5% of rates of longitudinal direction relaxation, heat treatment for 15 seconds was performed at 200 degrees C, and the oriented film was rolled round after cooling to the room temperature. The appearance of the obtained coated film did not have coloring, either, it was good and the coat layer was insoluble in water. The oxygen transmittance of a coated film and the oxygen transmission coefficient of a coat layer were shown in Table 1.

[0055] The coated film was obtained by the same actuation as an example 15 using the coat liquid of example 16 example 12 and this presentation. The oxygen transmittance of the obtained coated film and the oxygen transmission coefficient of a coat layer were shown in Table 1.

[0056] Using the extruder (the diameter of 75mm and ratio of length to diameter are the slow compression type monopodium screw of 45) equipped with the T die, example 17 nylon 6 resin was

extruded in the shape of a sheet at the cylinder temperature of 260 degrees C, and the T-die temperature of 270 degrees C, was stuck on the cooling roller adjusted by the skin temperature of 10 degrees C, was quenched, and was used as the unstretched film with a thickness of 150 micrometers. Then, the unstretched film was led to the gravure roll type coating machine, the coat liquid of the same presentation as an example 1 was coated so that the coat thickness after desiccation might be set to 20 micrometers, and it dried for 45 seconds in the 80-degree C hot blast dryer. Next, after supplying the film to the tenter type coincidence biaxial drawing machine and carrying out a preheating for 2 seconds at the temperature of 100 degrees C, it extended to the lengthwise direction at 170 degrees C, and extended by one 3.5 times the scale factor of this in 3 times and a longitudinal direction. Next, at 5% of rates of longitudinal direction relaxation, heat treatment for 15 seconds was performed at 200 degrees C, and the oriented film after cooling was rolled round to the room temperature. The appearance of the obtained coated film did not have coloring, either, it was good and the coat layer was insoluble in water. The oxygen transmittance of a coated film and the oxygen transmission coefficient of a coat layer were shown in Table 1.

[0057] The coated film was obtained by the same actuation as an example 17 using the coat liquid of example 18 example 12 and this presentation. The oxygen transmittance of the obtained coated film and the oxygen transmission coefficient of a coat layer were shown in Table 1.

[0058] The coated film was obtained by the same actuation as an example 1 except having set example 19 heat treatment for 1 minute and as for 5 minutes at 200 degrees C. Both coat thickness was 2 micrometers. The appearance of the obtained coated film did not have most coloring, it was good and the coat layer was insoluble in water. Moreover, the oxygen transmittance in 20 degrees C and 85%RH was 15, and 2 ml/m<sup>2</sup> and day-MPa, respectively, and the oxygen transmission coefficients of a coat layer were 31, and 4 ml-mu m/m<sup>2</sup> and day-MPa.

[0059] The coated film was obtained by the same actuation as an example 1 using the 10-% of the weight water solution of example of comparison 1PVA (UF040 whenever [ G and saponification ] made in Unitika Chemical, 99%, average degree of polymerization 400). The coat layer of the obtained coated film was dissolved in water. The oxygen transmittance of a coated film and the oxygen transmission coefficient of a coat layer were shown in Table 1.

[0060] Example of comparison 2PVA (UF040 whenever [ G and saponification ] made in Unitika Chemical, 99%, average degree of polymerization 400) was dissolved in pure water, and 10% of the weight of the water solution was obtained. Polyacrylic acid (Wako Pure Chem industrial company make, the 25 % of the weight water solution of polyacrylic acid, number average molecular weight 150000) was diluted with the water solution which contains five-mol % of a sodium hydroxide to the carboxyl group of polyacrylic acid, and it considered as 10% of the weight of the water solution. The water solution was mixed, it stirred and coat liquid was obtained so that the weight ratio of PVA and polyacrylic acid might become 70/30. The coated film was obtained by the same actuation as an example 1 using this coat liquid. The coat layer of the obtained coated film was dissolved in water. The oxygen transmittance of a coated film and the oxygen transmission coefficient of a coat layer were shown in Table 1.

[0061] The weight ratio of example of comparison 3PVA and polyacrylic acid was made into 30/70, and coat liquid was adjusted so that 5Eq might become % to the carboxyl group of polyacrylic acid. The coat was carried out by MEIYABA so that the paint film thickness after drying this coat liquid on a biaxial extension PET film (Emblet PET 12 by Unitika, Ltd., thickness of 12 micrometers) might be set to about 2 micrometers, and after drying for 2 minutes at 100 degrees C, it heat-treated for 15 seconds at 200 degrees C. The coat layer of the obtained coated film was dissolved in water. The oxygen transmittance of a coated film and the oxygen transmission coefficient of a coat layer were shown in Table 1.

[0062]

[Table 1]

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		コート剤							基材フィルム	コート層厚み (μm)	バリア性能	
		配合比(重量%)		中和度(当量%)	架橋剤		クニピアFの添加割合(重量部)	コートフィルムの酸素透過度			コート層の酸素透過係数	
		PVA	ポリマレイン酸共重合体		種類	添加量(重量部)						
実施例	1	70	30	5	—	—	—	PET	2.0	88	195	
	2	90	10	5	—	—	—	PET	2.0	95	212	
	3	30	70	5	—	—	—	PET	2.0	210	548	
	4	70	30	30	—	—	—	PET	2.0	80	176	
	5	70	30	5	アクリン	5	—	PET	1.9	58	118	
	6	70	30	5	スチレン	10	—	PET	2.0	65	140	
	7	70	30	5	イソシアネート	10	—	PET	2.1	72	184	
	8	70	30	5	尿素	5	—	PET	1.9	75	155	
	9	70	30	5	カルボジライト	3	—	PET	2.0	64	138	
	10	70	30	5	ジメチルジメチル塩	1	—	PET	2.0	68	147	
	11	70	30	0	—	—	—	PET	2.1	230	618	
	12	70	30	5	—	—	10	PET	2.0	2	4	
	13	70	30	5	アクリン	6	10	PET	2.0	2	4	
	14	70	30	5	—	—	—	ナイロン	2.0	78	171	
	15	70	30	5	—	—	—	PET	1.8	85	188	
	16	70	30	5	—	—	10	PET	2.0	33	69	
	17	70	30	5	—	—	—	ナイロン	2.0	80	200	
	18	70	30	5	—	—	10	ナイロン	1.9	30	62	
比較例	1	100	0	—	—	—	—	PET	2.0	460	1880	
	2	70	30 <sup>1)</sup>	5	—	—	—	PET	2.0	790	12900	
	3	30	70 <sup>1)</sup>	10	—	—	—	PET	1.9	830	21300	

(注)

比較例2、3における、エチレン-マレイン酸共重合体の値の1)はアクリル酸の重量%

イソシアネート：第一工業製薬社製 エラストロン BN-11

スチレン：東京化成社製 ブタンジオールジグリシジルエーテル

アクリン：三井サイテック社製 サイメル325

尿素：三井サイテック社製 UFR-65

カルボジライト：日清紡社製 カルボジライトE

ジメチルジメチル：第一希元素社製 ジルコゾールAC-7 (炭酸ジルコニウムアンモニウム)

[0063]

[Effect of the Invention] According to this invention, a water resisting property is good, and has gas barrier property high also under high humidity, and the thermoplastics film which can moreover be manufactured cheaply industrially is offered.

[Translation done.]